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- USSR -

By V. I. Spitsyn and V. G. Finikov

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A STUDY OF THE ISOTOPE EXCHANGE BETWEEN GASEOUS OXYGEN AND THE SALTS OF SOME ACIDS CONTAINING OXYGEN AT HIGH TEMPERATURES

[This is a translation of an article written by V. I. Spitsyn and V. G. Finikov in Problemy Kinetiki i Kataliza (Problems in Kinetics and Catalysis), IX, Izotopy v Katalize (Isotopes in Catalysis), Moscow, 1957, pages 264-266.]

The study of the velocity of the isotope exchange between the gaseous oxygen and the solid salts of an oxygen-containing acid presents considerable interest inasmuch as it permits evaluation of the bond energy in the above mentioned compounds. We investigated isotope exchange between gaseous oxygen and sulfates of alkali elements and also between sodium molybdate and carbonate with the purpose of comparing the stability of the oxygen bond in these salts. To conduct these experiments we used oxygen containing about 1.3% of the O^{18} atom. The exchange was carried out in an apparatus a description of which was published earlier [1]. The measurement of the O^{16} and O^{18} isotope content was conducted by the massspectrometer method. In experiments in excess of 7 hours, the following data was received relative to the relationship of the degree of exchange and the temperature.

Table 1

Isotope exchange between gaseous oxygen and sulfates of alkali elements (duration of exchange 7 hours.)

Conditions of experiment	Li_2SO_4			Na_2SO_4			K_2SO_4				Rb_2SO_4			Cs_2SO_4		
Temperature, C°	680	729	772	763	790	818	766	776	794	821	686	725	752	680	742	787
Degree of exchange, %	1,75	5,75	11,53	0,88	1,46	1,19	0,40	0,60	0,73	0,81	1,10	1,60	3,11	0,59	1,32	1,26

It should be noted that A. Kasatkina [2] was not able to find any isotope exchange between oxygen and potassium sulfate at temperatures of 500°.

To substantiate the correctness of our experimental data, it was important to determine the balance of O^{18} engaged in the exchange. In the cited article [1] this was accomplished only for sodium molybdate and carbonate, which, after exchange with gaseous oxygen, were dissolved in water. The oxygen exchange occurring between ions of salt and water of ordinary isotope composition permit us to determine the content of O^{18} in the salt. However, this method is inapplicable for sulfates because they do not exchange oxygen SO_4^{2-} with water. It is known that the sulfates of alkali elements are reduced by carbon at 1,100°, forming CO_2 at the expense of their own oxygen. However, this method presents considerable experimental difficulties when determining the isotope content of oxygen of the studied salts. We were successful in being able to reduce sulfates in an ordinary quartz apparatus at 600°, employing as a reducer potassium ferrocyanide: $K_4[Fe(CN)_6]$. This way it is possible to carry out not only partial but also complete reduction of sulfates. Complete reduction of some samples of sulfate after the experiments of exchange with oxygen was used by us for determination of the O^{18} balance. The results are presented in Table 2. Comparison of the cited numbers indicates that the value of the exchange degree shown in Table 1 were determined with an accuracy of 5 to 10%.

The velocity of the isotope exchange between the

solid sulfates and the gaseous oxygen depends to a considerable extent on the degree of dispersion of the original compounds. The determination of the specific surface of the studied sulfates by the method of unstationary diffusion flow and the average statistical size of crystals by means of a Debyl crystalgram brought concurrent results - 4.3 m^2/G for Li_2SO_4 and 1.5 m^2/G for all other sulfates.

For measurement of the strength of the oxygen bonds in the studied salts we used values of energy of the activating process of the isotope exchange and a specific exchange - the degree of exchange (in %), reached at the determination temperature for certain period of time related to 1 m^2 salt surface. Table 3 shows the corresponding figures.

Table 2

Comparison of isotope composition of oxygen sulfates measured by independent methods

Compound	Temp. of experimental exchange with oxygen, °C	Content of O^{18}, % atom	
		calculated according to changes in conposition of gas phase	found during reduction of solid phase
Li_2SO_4	729	0.250	0.253
Li_2SO_4	772	0.328	0.332
Rb_2SO_4	752	0.236	0.236

The energies of activation were calculated with an accuracy of plus or minus 10-15%, on the supposition that the limiting stage of the process occurs on the surface. The value of specific exchange is free from any kinetic suppositions. However, in view of insufficiently exact determination of the size of the specific surface and a relatively wide temperature interval (752-766°) for which it was calculated from the experimental data, it should be considered as a less exact characteristic for the activation energy. Comparison of the cited data of values in Table 3 compels us to conclude that the velocity of the oxygen isotope exchange of the studied sulfates depends on the nature of the alkali elements. This points out to variations in the degree of the strength of the oxygen bonds in investigated sulfates. Maximum energy of activation was noted for

potassium sulfate. The corresponding values of sodium and lithium sulfates on one hand and rubidium and cesium on the other hand legitimately decrease. This fact can be explained by examing the polarization interaction of atoms forming the studied sulfates [3]. A slightly polarized and relatively strongly polarizing ion of lithium exerts a counter polarizing effect on a nearby atom of oxygen, of the ion are weakened. The more stable are sulfates of sodium and potassium in which the ratio of polarizations of the oxygen atoms and the ions of the alkali element insures sufficient polarity of bonds between the alkali element and the ion. With reference to the voluminous and easily polarized ions of rubidium and cesium, the oxygen of the anion itself is capable of exerting a collective polarizing effect, and this is accompanied with weakening of the anion's "monolithic" condition.

Table 3

Compound	Energy of activation, k cal/mol	Specific exchange, % g/m^2
Li_2SO_4	89	2,2
Na_2SO_4	54	0,6
K_2SO_4	57	0,8
Rb_2SO_4	40	2,1
Cs_2SO_4	24	1,9

As far as specific exchange, its value is inversely proportional to the energy of activation. Analysis of figures in Table 3 confirms this. In accordance with the stated presentation it was to be expected that the increase of a central atom radius of anion should have been accompanied by the decrease of the stability of the oxygen bond and, as a consequence, an increase in the velocity of the isotope exchange. The decrease of the valence of the central atom also should exert a weakening on the monolithic state of the anion. Examples of study of the isotope exchange between gaseous oxygen and a sodium molybdate and carbonate substantiated these hypotheses. For sodium

molybdate, a degree of exchange equal to 18.0% was reached after 7 hours even at the temperature of 574°. In the case of sodium carbonate, for the same period of time at 753°, the degree of exchange was 47.3%. The greater radius of the molybdenum in an MoO_4^{2-} anion and a smaller valency of carbon in CO_3^{2-} anion in comparison with a series from the SO_4^{2-} anion lead to an increase in the mobility of the oxygen in the exchange reactions, and this indicates smaller stability of oxygen in Na_2MoO_4 and Na_2CO_3 in comparison with the corresponding sulfate.

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